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ELECTRONIC POLARIZABILITY OF OXYGEN AND VARIOUS CATIONS IN SELECTED TRICLINIC MINERALS: POINT-DIPOLE THEORY

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ABSTRACT

Point-dipole theory is used to calculate the indices of refraction and orientation of the optical indicatrix in selected triclinic minerals: kyanite, wollastonite, schizolite (Mn-rich pectolite), microcline, albite, walstromite ($BaCa_2Si_3O_9$), kaolinite, pyrophyllite-*1A*, talc-*1A*, and triclinic forms of clinochlore and chloritoid. Electronic polarizabilities for the constituent species (atoms and OH groups) are optimized for the best agreement between observed and calculated optical properties. As many as six electronic polarizabilities can be determined in this way for each mineral. The same cations in symmetrically distinct sites were assigned the same polarizability. Four kinds of oxygen atoms were distinguished according to coordination: bridging oxygen (T–O–T, T = Si or $^{[4]}$Al), nonbridging oxygen (T–O–X_n, X representing a cation other than Si, $^{[4]}$Al, or H), oxygen not bonded to Si, $^{[4]}$Al, or H (*i.e.*, O–X_n), and hydroxyl oxygen (H–O–X_n). The calculations show that the electronic polarizability of an atom (or OH group) depends on the local structural setting, *i.e.*, polarizabilities are site-specific. Electronic polarizabilities are not readily transferable and therefore not strictly additive.

Keywords: optical properties, point-dipole theory, electronic polarizabilities, triclinic minerals.

SOMMAIRE

La théorie des dipoles ponctuels sert à calculer les indices de réfraction et l'orientation de l'indicatrice optique de certains minéraux tricliniques: kyanite, wollastonite, schizolite (pectolite riche en Mn), microcline, albite, walstromite ($BaCa_2Si_3O_9$). kaolinite, pyrophyllite-1*A*, talc-1*A*, et les formes tricliniques du clinochlore et de la chloritoïde. Les polarisabilités électroniques des espèces présentes (atomes et groupes OH) sont optimisées pour obtenir la meilleure concordance entre propriétés optiques observées et calculées. On peut déterminer jusqu'à six polarisabilités électroniques de cette façon pour chaque espèce minérale. Les cations d'un seul élément impliqué dans des sites symétriquement distincts sont attribués la même polarisabilité. On distingue quatre sortes d'atomes d'oxygène selon leur coordinence: atome participant à une liaison T–O–T (T représente Si ou $^{[4]}$Al), atome participant à une liaison T–O–X_n (X représente un cation autre que Si, $^{[4]}$Al, ou H), atome d'oxygène non lié à Si, $^{[4]}$Al, ou H (*i.e.*, O–X_n), et atome d'oxygène associé à un groupe hydroxyle (H–O–X_n). D'après les calculs, la polarisabilité électronique d'un atome (ou d'un groupe OH) dépendrait des agencements structuraux locaux. C'est donc dire que les polarisabilités dépendent des sites structuraux. Les polarisabilités électroniques ne sont donc pas facilement transférables, ni strictement additives.

(Traduit par la Rédaction)

Mots-clés: propriétés optiques, théorie des dipoles ponctuels, polarisabilités électroniques, minéraux tricliniques.

INTRODUCTION

The point-dipole theory has been used successfully to calculate the orientation of the optical indicatrix in low-symmetry (monoclinic and triclinic) minerals. The approach used by Abbott (1993) was somewhat compromised by the limited size of a crystal structure (number of atoms in one unit cell) on which the calculations could be performed. For reasons related to the allocation of memory by the computer-program compiler, the theory could not be applied to structures with more than 28 sites in the unit cell. Calculations were done on large structures by taking advantage of the approximate additivity of electronic polarizabilities (Lasaga & Cygan 1982) and by describing the structures in terms of groups of atoms. Thus the structures used in the earlier calculations (Abbott 1993) were described in terms of the cation sites only, with the electronic polarizability of the anions distributed over the cation sites. Using electronic polarizabilities that are linear combinations of published values (Lasaga & Cygan 1982), the results were found to be surprisingly successful in reproducing the orientation of the optical indicatrix in kyanite, wollastonite, and various feldspars. Unfortunately, the calculated principal indices of refraction were in most cases not altogether satisfactory.

This paper presents results using a modified version of the computer program, capable of performing calculations on structures with as many as 40 sites in the unit cell. Calculations were performed on selected triclinic minerals (Table 1). The relatively small number of minerals in the study was dictated by the following constraints: (1) less than 40 sites in the unit cell, (2) simple chemistry, (3) known structure, and (4) known optical properties. All atomic sites, except those occupied by hydrogen, were included in the calculations. Triclinic minerals are of special interest because the orientation of the optical indicatrix is not constrained by symmetry.

Whereas linear combinations of published electronic polarizabilities were used (Lasaga & Cygan 1982) and not allowed to vary in the previous calculations (Abbott 1993), in this study the electronic polarizabilities were optimized so as to minimize the discrepancy between observed and calculated optical properties (principal indices of refraction and orientation of the indicatrix). In this way, it is possible to determine as many as six electronic polarizabilities, the number corresponding to the degrees of freedom in the refractive properties for a given wavelength of incident light. For a triclinic mineral, there are three degrees of freedom associated with the principal indices of refraction, and another three degrees of freedom associated with the principal directions of vibration (*i.e.*, orientation of the indicatrix). The objectives are (1) to calculate the optical properties using complete structures of minerals, (2) to calculate optimized electronic polarizabilities, and (3) for each type of atom, but mainly for oxygen, to compare optimized electronic polarizabilities in different structural settings.

TABLE 1. TRICLINIC MINERALS USED IN CALCULATIONS

MINERAL	STRUCTURE DETERMINATION	OPTICAL PROPERTIES
Kyanite	Winter & Ghose (1979)	Deer *et al.* (1985)
Wollastonite	Ohashi (1984)	Deer *et al.* (1985)
Schizolite*	Ohashi *et al.* (1978)	Deer *et al.* (1985)**
Microcline	Blasi *et al.* (1987)	Deer *et al.* (1985), Winchell & Winchell (1951)
Albite	Armbruster *et al.* (1990)	Deer *et al.* (1985), Winchell & Winchell (1951)
Walstromite	Dent Glasser & Glasser (1968)	Alfors *et al.* (1965)
Pyrophyllite	Lee & Guggenheim (1979)	Deer *et al.* (1985)
Kaolinite	Bish & von Dreele (1989)	Deer *et al.* (1985)
Talc	Perdikatsis & Burzlaff (1981)	Deer *et al.* (1985)
Clinochlore	Joswig & Fuess (1990)	Deer *et al.* (1985)
Chloritoid	Hanscom (1980)	Deer *et al.* (1985), Phillips & Griffen (1981)

* Mn-rich pectolite.
** Optical properties referred to pectolite.

THEORY AND METHOD

For a given frequency of light, the wavelength in an anisotropic crystal (hence index of refraction) can be calculated from a knowledge of the structure and the electronic polarizabilities of the species making up the structure (Abbott 1993, Pohl 1978, Pohl & Rath 1979, Lager *et al.* 1987). According to the point-dipole theory, as extended by Abbott (1993), the relationship among structure, electronic polarizability, and refraction of light can be summarized conveniently in four equations. The first equation (Cummins *et al.* 1976, Pohl 1978) gives the local electric field, **F**(k), at site k as a function of the local electric fields at all sites, k′, in the unit cell,

$$\mathbf{F}(\mathrm{k}) = \mathbf{E} + (1/V)\Sigma_{\mathrm{k}'}\, \mathrm{L}(\mathrm{kk}')\, \alpha_{\mathrm{p}}(\mathrm{k}')\, \mathbf{F}(\mathrm{k}'). \qquad (1)$$

The vector **E** is the macroscopic (externally applied) electric field, L(kk′) is the Lorentz factor tensor for the pair k–k′, $\alpha_p(k')$ is the electronic polarizability of species k′, and V is the volume of the unit cell. The macroscopic electric field, **E**, is equated with the vibration direction (hence plane of polarization) of the incident light. The Lorentz factor tensors, L(kk′), depend only on the geometry of the structure, and were calculated using the method of Cummins *et al.* (1976). The polarizabilities, $\alpha_p(k')$, are usually determined empirically (Lasaga & Cygan 1982, Jaffe 1988). Equation 1 forms a system of linear equations solvable for the individual local electric fields, **F**(k).

The dielectric susceptibility tensor, χ, is then obtained from the local electric fields (Pohl 1978):

$$\chi\mathbf{E} = (1/V)\, \Sigma_{\mathrm{k}}\, \alpha_{\mathrm{p}}(\mathrm{k})\, \mathbf{F}(\mathrm{k}) \qquad (2)$$

Referred to a Cartesian base, **x** (column matrix of coordinate variables x, y, and z), the coefficients of the dielectric susceptibility tensor describe the surface of an ellipsoid,

$$\mathbf{x}^{\mathrm{T}}\, \chi\, \mathbf{x} = 1. \qquad (3)$$

The principal axes of the ellipsoid are parallel to the principal axes of the optical indicatrix. The directions of the principal axes and their magnitudes (eigenvectors and eigenvalues, respectively) are found by diagonalizing the dielectric susceptibility tensor (*e.g.*, Julian & Bloss 1987). The principal indices of refraction are then simply related to the eigenvalues, χ_{ii},

$$n_{\mathrm{i}} = (\chi_{\mathrm{ii}} + 1)^{1/2}, \qquad (4)$$

where values of n_i (i = 1, 2, 3) correspond to indices of refraction α, β, and γ.

The quantity $\chi_{ii} + 1$ is the familiar dielectric constant. All calculations were referred to the D wavelength ($\lambda_D = 5893$ Å).

The possibility of useful relationships with other optical constants may not have eluded the diligent reader. The relationship of popular optical constants (*i.e.*, Gladstone–Dale, Drude, and specific refractivity) to equations 2 and 4 is discussed in the Appendix.

Calculations were done using the computer program OPT, written in TURBO PASCAL by the author for an IBM-compatible PC. The program uses the Ewald method of lattice summations, as formalized by Cummins *et al.* (1976), and various subroutines and numerical methods documented by Cooper (1981) and Boisen & Gibbs (1985). The program is available from the author.

Calculating Lorentz factor tensors consumes most of the computing time, and storing them, for rapid retrieval, can require large amounts of memory. In this latest version of the program, the maximum number of sites in the unit cell is 40. This limitation is imposed by the memory allocation (stack size) of the TURBO PASCAL compiler.

Electronic polarizabilities were optimized by varying the individual values so as to minimize the discrepancy between observed and calculated optical properties. Whereas optimization has been shown to be amenable to the method of least squares if applied to structures more symmetrical than monoclinic (Lager *et al.* 1987), in the present calculations (applied to triclinic structures), each cycle of calculation of refractive properties with a new set of polarizabilites requires a large amount of computing time. Exploratory efforts to understand the behavior of the variables during optimization indicated that a simple manual search was adequate, both with regard to expected levels of precision and reasonable agreement with observed optical properties. The strategy starts with nominal values for the polarizability of the cations and the same polarizability for each oxygen atom. Starting values for electronic polarizabilities were generally taken from Lasaga & Cygan (1982). The one value for $\alpha_p(O)$ was varied until the mean of the calculated indices of refraction matched the mean of the observed indices of refraction. Then the birefringences (γ–β and β–α) were adjusted by varying the individual polarizabilities until the best agreement was obtained between calculated and observed optical properties (indices of refraction and orientation of the optical indicatrix). Results thus obtained appear to be unique insofar as no further improvement was produced by any small departures of the electronic polarizabilities from the final values, *i.e.*, the final electronic polarizabilities correspond to a true minimum in the discrepancy between observed and calculated optical properties. In no case did exploratory efforts indicate a second (or third, *etc.*) independent minimum.

During the course of such calculations on different minerals, it became apparent that satisfactory results could not be obtained without making some distinction (in terms of electronic polarizability) between atoms of a given element occupying symmetrically distinct sites. This contradicts strict additivity of the electronic polarizabilities, admittedly a very approximate relationship (Lasaga & Cygan 1982). Pohl and co-workers (Pohl 1978, Pohl *et al.* 1978, Pohl & Rath 1979) have shown that the electronic polarizability for a given atom depends on the local structural setting. This is partly reflected in the different values reported by various investigators for electronic polarizabilities of selected elements (Jaffe 1988, Pohl 1978, Pohl *et al.* 1978, Pohl & Rath 1979). Additivity is supported only insofar as the range of electronic polarizabilities reported for a given element is generally small.

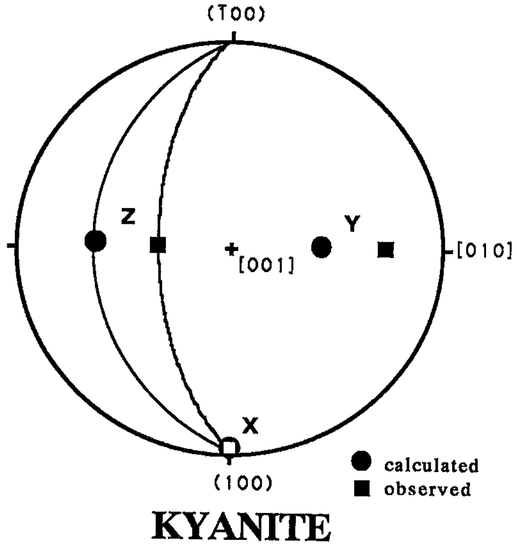
With the hopeful intention of preserving some vestige of additivity, oxygen atoms were distinguished in a general way according to coordination. Four types of oxygen atoms were recognized: (1) "Ob" oxygen atoms bridging two tetrahedrally coordinated cations (T–O–T), (2) "Onb" nonbridging oxygen atoms coordinated to one tetrahedrally coordinated cation (Si, Al) and non-tetrahedrally coordinated cations (T–O–X_n), (3) "Ox" oxygen atoms coordinated to neither tetrahedrally coordinated cations nor hydrogen (O–X_n), and (4) "Oh" oxygen atoms coordinated to hydrogen (H–O–X_n). This strategy, or compromise, proved to be satisfactory and more amenable to the identification of general trends than adopting the extreme position of assigning a different electronic polarizability to each symmetrically independent oxygen atom. For a given structure, symmetrically distinct cations of the same element were assigned the same electronic polarizability.

The hydrogen ion, having no electrons, is not polarizable. However, the presence of H^+ no doubt has a profound effect on the polarizability of hydroxyl oxygen, both with regard to the magnitude and anisotropy of the polarizability (Bunn 1961). The influence of hydrogen atoms is difficult to model in point-dipole theory. Here, hydrogen sites are ignored, and the hydroxyl group is treated as a single polarizable species centered at the oxygen site.

RESULTS

Kyanite

The results on kyanite are reported in Figure 1. The structure determination used in the calculations (Winter & Ghose 1979) pertains to kyanite of unknown, but presumably near-end-member, composition. The calculated and observed directions of vibration are illustrated in the cyclographic projection, where X, Y, and Z correspond, respectively, to the α, β, and γ indices of refraction. The observed indices of refraction (Fig. 1) are for kyanite of unknown, but presumably near-end-member, composition (Deer *et al.* 1985). The calculated indicatrix is misoriented by



α_p(Si) = 0.00 (0.08) $Å^3$
α_p(Al) = 0.25 (0.13)
α_p(Onb) = 1.35 (1.31)
α_p(Ox) = 0.95 (1.31)

α = 1.713 (1.712)
β = 1.719 (1.721)
γ = 1.727 (1.727)

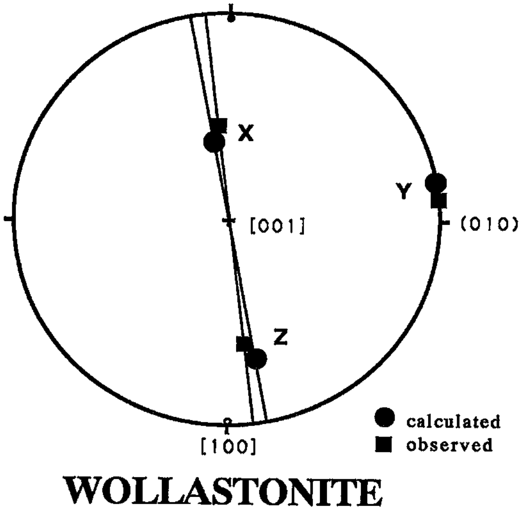
FIG. 1. Kyanite: cyclographic projection of calculated and observed directions of vibration. Optimized electronic polarizabilities (values in parentheses, from Lasaga & Cygan 1982). Calculated and observed (in parentheses) indices of refraction. References for observed directions of vibration and observed indices of refraction are listed in Table 1.

about 25° with respect to rotation about the X vibration direction. By adjusting the polarizabilities, the indicatrix could be made to reorient to within 10° of the observed orientation, but not without causing unacceptably large errors in the calculated indices of refraction. All three calculated indices of refraction agree well with observed values. The optimized electronic polarizabilities (Fig. 1) can be compared with values tabulated by Lasaga & Cygan (1982). No combination of polarizabilities with a nonzero value for α_p(Si) improved the results. The good agreement between observed and calculated refractive properties was achievable only by acknowledging a significant distinction between the electronic polarizabilities of oxygen atoms coordinated to Si (Onb, O–$SiAl_2$) and oxygen atoms coordinated only to Al (Ox, O–Al_4).

Wollastonite and schizolite

Figure 2 shows the results on wollastonite. The structure determination used in the calculations was for near-end-member wollastonite, $(Ca_{1.002}Fe_{0.005}Mn_{0.002}Mg_{0.03})Si_{0.994}O_3$ (Ohashi 1984). Calculated directions of vibration plot very close to (within 5° of) the corresponding observed directions of vibration in the cyclographic projection; calculated and observed indices of refraction are in close agreement. The observed indices of refraction (Fig. 2) are for wollastonite of composition $(Ca_{0.988}Fe_{0.001}Mn_{0.001}Mg_{0.007})(Si_{0.996}Fe_{0.003}Al_{0.003})O_3$ (Deer *et al.* 1985).

In wollastonite, all oxygen atoms are either bridging or nonbridging. The results were greatly improved by recognizing two types of nonbridging oxygen atoms. These are distinguishable on the basis of the number of nearest-neighbor Ca atoms, O–$SiCa_2$ and O–$SiCa_3$, with the latter configuration having the lower electronic polarizability for the oxygen. The polarizability of the bridging oxygen atoms was significantly lower than the polarizabilities of either type of the nonbridging oxygen atoms. The value for α_p(Ca) is substantially lower than that reported by Lasaga & Cygan (1982). No improvement in the



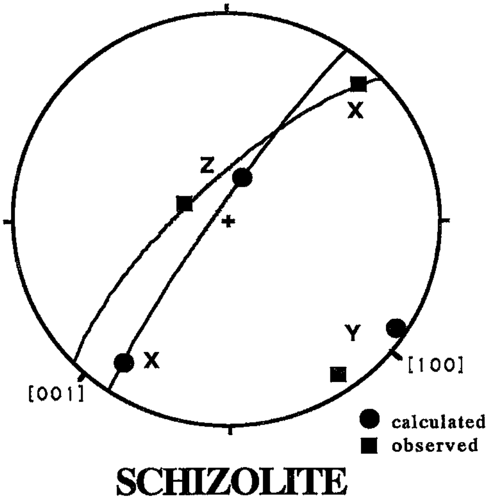
α_p(Si) = 0.11 (0.08) $Å^3$
α_p(Ca) = 1.03 (1.66)
α_p(Ob) = 1.23 (1.31)
α_p(Onb) = 1.55 (1.31)
α_p(Onb) = 1.46 (1.31)

α = 1.618 (1.618)
β = 1.625 (1.628)
γ = 1.630 (1.631)

FIG. 2. Wollastonite: cyclographic projection of calculated and observed directions of vibration. Optimized electronic polarizabilities (values in parentheses, from Lasaga & Cygan 1982). Calculated and observed (in parentheses) indices of refraction. References for observed directions of vibration and observed indices of refraction are listed in Table 1.

results could be produced with any combination of assigned polarizabilities involving α_p(Ca) greater than approximately 1.05 Å^3.

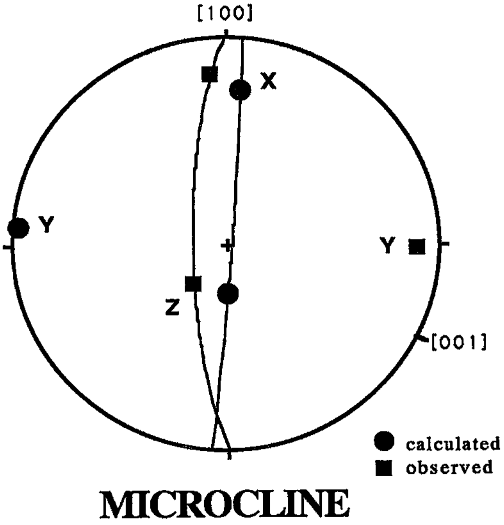
The results on schizolite (an Mn-rich variety of pectolite) are given in Figure 3. The structure determination used in the calculations was for schizolite of composition $Na(Ca_{1.226}Mn_{0.638}Fe_{0.136}Mg_{0.000})HSi_3O_9$ (Ohashi & Finger 1978). Agreement between observed and calculated refractive properties is not quite as good as for wollastonite, although it should be noted that the comparison here is with the observed indices of refraction reported for a non-end-member pectolite of unknown composition and observed directions of vibration for presumed end-member pectolite (Deer *et al.* 1985). The calculated value for γ is notably too low, and apparently not correctable by varying the polarizabilities. The optimized polarizabilities are comparable to values for comparable atomic sites in wollastonite. The role of the hydrogen atoms in pectolite is not entirely resolved (Ohashi & Finger 1978), but they are considered to be associated with the second type of bridging oxygen, with the lower electronic polarizability.



α_p(Si) = 0.11 (0.08) Å^3
α_p(Ca) = 1.12 (1.66)
α_p(Na) = 0.64 (1.14)
α_p(Ob) = 1.13 (1.31)
α_p(Onb) = 1.43 (1.31)
α_p(Onb) = 1.34 (1.31)

α = 1.609 (1.610)
β = 1.615 (1.615)
γ = 1.620 (1.645)

FIG. 3. Schizolite (Mn-rich pectolite): cyclographic projection of calculated and observed directions of vibration. Optimized electronic polarizabilities (values in parentheses, from Lasaga & Cygan 1982). Calculated and observed (in parentheses) indices of refraction. References for observed directions of vibration and observed indices of refraction are listed in Table 1.



α_p(K) = 0.99 (1.98) Å^3
α_p(Si) = 0.00 (0.08)
α_p(Al) = 0.00 (0.13)
α_p(Ob) = 1.46 (1.31)

α = 1.513 (1.514)
β = 1.516 (1.518)
γ = 1.527 (1.521)

FIG. 4. Microcline: cyclographic projection of calculated and observed directions of vibration. Optimized electronic polarizabilities (values in parentheses, from Lasaga & Cygan 1982). Calculated and observed (in parentheses) indices of refraction. References for observed directions of vibration and observed indices of refraction are listed in Table 1.

Microcline and albite

In *C*-centered feldspars, there are 52 atomic sites in the unit cell, exceeding by 12 the maximum number of 40 sites acceptable in the computer program. In order to reduce the number of sites per unit cell in the feldspars, cell parameters and atomic coordinates were expressed in terms of a primitive unit-cell consistent with the following transformation:

$$\begin{vmatrix} a' \\ b' \\ c' \end{vmatrix} = \begin{vmatrix} 1 & 0 & 0 \\ -0.5 & 0.5 & -1 \\ 0 & 0 & 1 \end{vmatrix} \begin{vmatrix} a \\ b \\ c \end{vmatrix} \qquad (5)$$

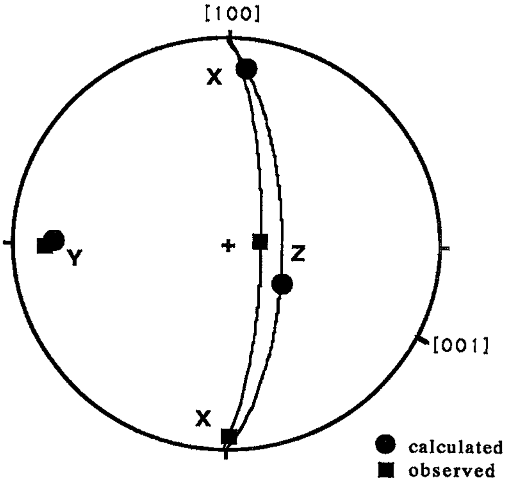
This reduces the number of species per unit cell by one-half. The results were then referred back to the standard *C*-centered geometry of the unit cell.

The structure determination used in the calculations was for microcline of composition $(K_{0.935}Na_{0.061}Rb_{0.002})AlSi_3O_8$ (Blasi *et al.* 1987). The results given in Figure 4 for microcline were obtained with polarizabilities determined by Pohl (pers. comm.). In this case, the polarizabilities were not optimized. The calculated optical properties were compared with those observed (Fig. 4) for end-member microcline (Winchell & Winchell 1951). Note that α_p(K) used in the calculations is half the value reported by Lasaga & Cygan (1982), and this difference is compensated by a somewhat higher α_p(Ob). The results could not be improved by changing the values for α_p(K) and α_p(O). Similarly, no combination of assigned polarizabilities with nonzero values for α_p(Si) or α_p(Al) improved the agreement. For practical purposes, the optical properties of microcline (and albite, Fig. 5) are determined by the oxygen and potassium (or sodium) atoms.

Results on albite are given in Figure 5. The structure determination used in the calculations was for an albite of approximate composition $(Na_{0.999}Ca_{0.001})Al_{1.001}Si_{2.999}O_8$ (Armbruster *et al.* 1990). The calculated optical properties were compared with those observed (Fig. 5) for end-member albite (Winchell & Winchell 1951). The optimized α_p(Ob) used in the calculations is similar to that used in microcline. The optimized α_p(Na) is significantly lower than the value offered by Lasaga & Cygan (1982). Again, as for microcline, $\alpha_p(Si) = \alpha_p(Al) = 0.0$ worked best.

Walstromite

Walstromite $(BaCa_2Si_3O_9)$ is a cyclosilicate with three-membered rings of SiO_4 tetrahedra. Results on this unusual structure are given in Figure 6. The structure determination used in the calculations was for walstromite of unknown, but presumably near-end-member composition (Dent Glasser & Glasser 1968). The calculated optical properties were compared with those observed (Fig. 6) for near-end-member walstromite (Alfors *et al.* 1965). Calculated and observed directions of vibration agree reasonably well, as do calculated and observed values for β and γ. The low calculated value for α seems not to be correctable by varying the polarizabilities. This problem and the unusually high value for α_p(Si) may be related to the necessarily strained articulation of the three-member ring of SiO_4 tetrahedra. Alternatively, the

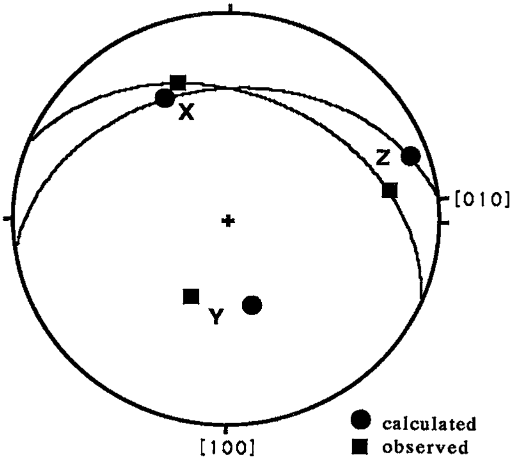


ALBITE

α_p(Na) = 0.64 (1.14) Å^3
α_p(Si) = 0.00 (0.08)
α_p(Al) = 0.00 (0.13)
α_p(Ob) = 1.42 (1.31)

α = 1.529 (1.527)
β = 1.531 (1.531)
γ = 1.538 (1.538)

FIG. 5. Albite: cyclographic projection of calculated and observed directions of vibration. Optimized electronic polarizabilities (values in parentheses, from Lasaga & Cygan 1982). Calculated and observed (in parentheses) indices of refraction. References for observed directions of vibration and observed indices of refraction are listed in Table 1.



WALSTROMITE

α_p(Si) = 0.32 (0.08) Å^3
α_p(Ca) = 1.90 (1.66)
α_p(Ba) = 2.60 (3.93)
α_p(Ob) = 1.47 (1.31)
α_p(Onb) = 0.93 (1.31)

α = 1.633 (1.668)
β = 1.682 (1.684)
γ = 1.687 (1.685)

FIG. 6. Walstromite: cyclographic projection of calculated and observed directions of vibration. Optimized electronic polarizabilities (values in parentheses, from Lasaga & Cygan 1982). Calculated and observed (in parentheses) indices of refraction. References for observed directions of vibration and observed indices of refraction are listed in Table 1.

anomalous value for α_p(Si) may be an artifact of a poorly determined structure (R = 0.16, Dent Glasser & Glasser 1968). The value for α_p(Ba) is compatible with high values reported by Pohl (1978) and inferred from Lasaga & Cygan (1982).

Kaolinite, pyrophyllite, talc, clinochlore

In order to reduce the number of sites per unit cell in the phyllosilicates, cell parameters and atomic coordinates were expressed in terms of a primitive unit-cell consistent with the following transformation:

$$\begin{vmatrix} a' \\ b' \\ c' \end{vmatrix} = \begin{vmatrix} 1 & 0 & 0 \\ -0.5 & 0.5 & 0 \\ 0 & 0 & 1 \end{vmatrix} \begin{vmatrix} a \\ b \\ c \end{vmatrix} \qquad (6)$$

The results were then referred back to the standard C-centered unit cell (Table 2).

Except as noted in Table 2 for the clinochlore, the structure determinations used in the calculations (Table 1) were for near-end-member compositions. Also, except for the clinochlore, the calculated optical properties were compared with those observed (Table 2) for end-member compositions (Deer *et al.* 1985). The observed optical properties (Table 2) for clinochlore pertain to a hypothetical mid-range composition of clinochlore (Fig. 82 in Deer *et al.* 1985). Indices of refraction and the orientation of the optical indicatrix were reasonably well reproduced in each case. The most significant departure from observed relationships was with regard to pyrophyllite, for which the calculated orientation of the optical indicatrix was rotated approximately 24° about c^* relative to the observed orientation. The problem could not be corrected by varying the polarizabilities in any way. Appropriate polarizabilities for hydroxyl groups in dioctahedral phyllosilicates seem to be lower than values for trioctahedral phyllosilicates. Except for clinochlore, α_p(Ob) and α_p(Onb) are the same and fairly restricted (1.25 or 1.28 Å^3) in the phyllosilicates.

TABLE 2. OPTIMIZED POLARIZABILITIES AND CALCULATED* OPTICAL PROPERTIES FOR TRICLINIC PHYLLOSILICATES

	KAOLINITE	PYROPHYLLITE	TALC	CLINOCHLORE
α_p(Si), Å^3	0.0	0.0	0.0	0.0
α_p($^{[6]}$Al)	0.26	0.65	--	--
α_p(Mg)	--	--	0.53	0.2**
α_p(Ob)	1.25	1.28	1.28	1.47
α_p(Onb)	1.25	1.28	1.28	1.47
α_p(Oh), inner#	1.23	1.10	1.55	1.47
α_p(Oh), surf.#	1.25	--	--	1.47
angle, X ^ c (°)	19.3 (10)	15.0 (10)	9.6 (10)	24.9 (4.5-7)
angle, Y ^ a	5.7 (1-3.5)	23.1 (0)	3.0 (0)	0.8 (0-2.5)
angle, Z ^ b	0.8 (0)	24.6 (0)	2.8 (0)	6.7 (0)
α ‖ X	1.547 (1.553)	1.558 (1.552)	1.536 (1.539)	1.573 (1.581)
β ‖ Y	1.559 (1.559)	1.590 (1.588)	1.590 (1.589)	1.591 (1.581)
γ ‖ Z	1.560 (1.560)	1.601 (1.600)	1.591 (1.589)	1.592 (1.586)

* Observed values in parentheses. See Table 1 for references.
** Sites actually occupied by Mg + Al.
\# Inner = pyrophyllite-like OH in kaolinite, OH of talc-like sheet in clinochlore. Surf(ace). = gibbsite-like OH in kaolinite, OH of brucite-like sheet in clinochlore.

TABLE 3. OPTIMIZED POLARIZABILITIES AND CALCULATED* OPTICAL PROPERTIES IN TRICLINIC CHLORITOID

α_p(Si), Å^3	0.0
α_p($^{[6]}$Al)	0.25
α_p(Fe)	0.30
α_p(Onb)	1.40
α_p(Ox)	1.26
α_p(Oh)	1.54
angle, X ^ c (°)	9.2 (~0)
angle, Y ^ b	38.4 (~0)
angle, Z ^ a	37.0 (~0)
α ‖ X	1.704 (1.713)
β ‖ Y	1.715 (1.719)
γ ‖ Z	1.723 (1.723)

* Observed values in parentheses. See Table 1 for references.

Thus in phyllosilicates, except for chlorite-group minerals, the polarizability of oxygen appears to be transferable.

Chloritoid

In order to reduce the number of sites per unit cell in chloritoid, cell parameters and atomic coordinates were expressed in terms of a primitive unit-cell consistent with the following transformation:

$$\begin{vmatrix} a' \\ b' \\ c' \end{vmatrix} = \begin{vmatrix} 0.5 & -0.5 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix} \begin{vmatrix} a \\ b \\ c \end{vmatrix} \qquad (7)$$

The results of the calculations were then referred back to the standard C-centered unit cell (Table 3).

The structure determination used in the calculations pertains to chloritoid of composition $(\mathrm{Fe}^{2+}_{1.77}\mathrm{Mg}_{0.10}\mathrm{Mn}_{0.03})\mathrm{Al}_{3.93}\mathrm{Fe}^{3+}_{0.11}\mathrm{Si}_{2.03}\mathrm{O}_{10}(\mathrm{OH})_{3.82}$ (Hanscom 1980). The calculated optical properties were compared with those observed (Table 3) for chloritoid of unknown composition (Deer *et al.* 1985). The calculated orientation of the X vibration direction is approximately correct, but, like in pyrophyllite, the calculated indicatrix was rotated about c^* (close to the X vibration direction) by 38° from the correct alignment. Calculated indices of refraction are acceptably close to observed values.

DISCUSSION

The point-dipole theory as applied here treats each atom as though its polarizability were the same in all directions, *i.e.*, individual polarizabilities are isotropic. Lager *et al.* (1987) pointed out that discrepancies between calculated and observed indices of refraction

TABLE 4. SUMMARY OF OPTIMIZED ELECTRONIC POLARIZABILITIES

	A*	B	C	D	E	F	G	H	I	J	K	L&C
α_p(Si), Å^3	0.0	0.11	0.11	0.0	0.0	0.32	0.0	0.0	0.0	0.0	0.0	0.08
α_p($^{[4]}$Al)	--	--	--	0.0	0.0	--	--	--	--	--	--	0.13
α_p($^{[6]}$Al)	0.25	--	--	--	--	--	0.26	0.65	--	--	0.25	0.13
α_p(Mg)	--	--	--	--	--	--	--	--	0.53	0.2**	--	0.48
α_p(Fe)	--	--	--	--	--	--	--	--	--	--	0.30	1.66
α_p(Ca)	--	1.03	1.12	--	--	1.9	--	--	--	--	--	1.66
α_p(K)	--	--	--	0.99	--	--	--	--	--	--	--	1.98
α_p(Na)	--	--	0.64	--	0.64	--	--	--	--	--	--	1.14
α_p(Ba)	--	--	--	--	--	2.6	--	--	--	--	--	3.93
α_p(Ob)	--	1.23	1.13	1.46	1.42	1.47	1.25	1.28	1.28	1.47	--	1.31
α_p(Onb)	1.35	1.55	1.43	--	--	0.93	1.25	1.28	1.28	1.47	1.40	1.31
		1.46	1.33									1.31
α_p(Ox)	0.95	--	--	--	--	--	--	--	--	--	1.26	1.31
α_p(Oh) inner	--	--	--	--	--	--	1.23	1.10	1.55	1.47	--	--
α_p(Oh) surf.	--	--	--	--	--	--	1.25	--	--	1.47	--	--
α_p(Oh)	--	--	--	--	--	--	--	--	--	--	1.54	--

* A = kyanite, B = wollastonite, C = schizolite, D = microcline, E = albite, F = walstromite, G = kaolinite, H = pyrophyllite, I = talc, J = clinochlore, K = chloritoid. See Table 1 for references.
L&C = Values from Lasaga & Cygan (1982), except α_p(Fe) and α_p(Ba), which are inferred from Lasaga & Cygan (1982, Table 1).

** Sites occupied by Mg + Al.

may be due in large part to the use of isotropic polarizabilities. In the present calculations, discrepancies that might otherwise arise from this effect may be compensated wholly or in part by exaggerated values for one or more of the optimized polarizabilities. Given the generally good agreement between calculated and observed optical properties, the problem would be difficult to recognize.

Table 4 summarizes the optimized electronic polarizabilities. For a given element, the range of values indicates that polarizability depends on the local structural setting, *i.e.*, polarizabilities are site-specific. Even for an element having similar coordination in different minerals, polarizabilities can be very different. Transferability to other structures presumes some systematic relationship between polarizability and one or more site-specific properties, for instance site potential. Unfortunately, the limited data-base offers little more than vague generalities. With regard to site potential (Smyth & Bish 1988, Smyth 1989), there is no recognizable systematic relationship.

Tetrahedrally coordinated Si or Al have, for practical purposes, zero polarizability, except in wollastonite, schizolite, and walstromite. The exceptions are perhaps noteworthy for having unusually distorted SiO_4 tetrahedra. Octahedrally coordinated Al has a polarizability of 0.25 or 0.26 Å^3, except in pyrophyllite, for which good results could be obtained only by using a significantly elevated value for α_p($^{[6]}$Al), 0.65 Å^3. This may be a case where the elevated α_p($^{[6]}$Al) compensates for anisotropic polarizability of the OH group. The polarizability for Ca is 1.03–1.22 Å^3, except in walstromite, for which the best value for α_p(Ca) was found to be approximately 1.9 Å^3. In all three minerals with Ca, α_p(Ca) is significantly different from the value of 1.66 Å^3 reported by Lasaga & Cygan (1982). The polarizabilities for Na (0.64 Å^3) and K (0.98 Å^3) are approximately half of the respective values reported by Lasaga & Cygan (1982). In microcline and albite, calculations using the values of Lasaga & Cygan (1982) for α_p(K) and α_p(Na), together with their values for α_p(Si), α_p(Al) and α_p(O) (Table 4), produce incorrect indices of refraction (microcline: $\alpha = 1.520$, $\beta = 1.524$, $\gamma = 1.550$; albite: $\alpha = 1.527$, $\beta = 1.540$, $\gamma = 1.546$), and none of the calculated directions of vibration are closer than approximately 35° to the observed directions. For other cations (Mg, Fe, Ba), polarizabilities are less than values reported by, or inferred from, Lasaga & Cygan (1982), but consistent with other determinations (Jaffe 1988).

In Table 4, there are 22 polarizabilities for oxygen (excluding hydroxyl oxygen). The average value is 1.32 Å^3 (standard deviation: 0.16 Å^3), which is close to the value of 1.31 Å^3 reported by Lasaga & Cygan (1982). However, the range of optimized polarizabilities indicates clearly that the average value will not work well for any one of the minerals. The polarizability of oxygen is site-specific, and there is significant variation from one site to another. Table 4 affords few useful generalities regarding the variability of α_p(O). Polarizabilities for bridging oxygen atoms show a bimodal distribution, 1.13–1.28 Å^3 and 1.42–1.47 Å^3. The lower mode includes oxygen atoms in wollastonite, pectolite, and phyllosilicates (except clinochlore); the higher mode includes oxygen atoms in the feldspars, walstromite and clinochlore. Polarizabilities of nonbridging oxygen atoms range from 0.93 Å^3 in walstromite to 1.47 Å^3 in clinochlore. In each of the phyllosilicates, the polarizabilities for bridging and nonbridging oxygen atoms were found to be the same. In other minerals having both bridging and nonbridging oxygen atoms (wollastonite, schizolite, walstromite), the polarizabilities are different. In wollastonite and schizolite, the α_p(Ob) is less than α_p(Onb), whereas in walstromite, α_p(Ob) is greater than α_p(Onb). Only two of the minerals, kyanite and chloritoid, have oxygen atoms that are shared with neither Si nor H. In these minerals, α_p(Ox) is quite different, 0.95 Å^3 in kyanite, and 1.26 Å^3 in chloritoid.

Polarizabilities for hydroxyl groups range from 1.10 Å^3 in pyrophyllite to 1.55 Å^3 in talc. Lower polarizabilities are associated with the dioctahedral phyllosilicates, and there appears to be little difference between polarizabilities for inner (pyrophyllite-like) and surface (gibbsite-like) hydroxyl groups. The higher polarizabilities are associated with trioctahedral phyllosilicates, and again there appears to be little difference between the polarizabilities of inner (talc-like) and surface (brucite-like) groups of hydroxyl.

CONCLUSIONS

1. Electronic polarizabilities can be determined by minimizing the discrepancy between calculated and observed optical properties. Using optimized elec-

tronic polarizabilities, the optical properties calculated for triclinic minerals (indices and orientation of the optical indicatrix) are very close to observed optical properties.

2. Optimized electronic polarizabilities for atoms of a given element vary significantly depending on the local structural setting. Thus electronic polarizabilities are not readily transferable. Electronic polarizabilities may be transferable within a mineral group (*e.g.*, feldspars, dioctahedral phyllosilicates, *etc.*), but even then, only with considerable caution.

3. Earlier work (Abbott 1993) shows, and the present calculations confirm, that the essential information for the orientation of the optical indicatrix is contained in the Lorentz factor tensors; hence the orientation depends firstly on the geometry of the structure. The effect on the orientation of the optical indicatrix of varying the distribution of polarizability over the atomic sites only becomes important where the calculated birefringence is small. This caveat to an earlier conclusion (Abbott 1993) follows directly from the behavior of the orientation of the indicatrix during the optimization procedure.

Note added in proof: Results presented in this paper have been tested with a new computer program, OPTRFN, developed by (and available from) the author. Using the method of least squares, the program searches for the set of electronic polarizabilities that gives the least discrepancy between observed and calculated optical properties. For each mineral, the program confirms that the electronic polarizabilities (±0.02 Å^3) determined here do indeed correspond to a minimum discrepancy between observed and calculated optical properties.

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APPENDIX:
DRUDE CONSTANT, GLADSTONE–DALE CONSTANT, SPECIFIC REFRACTIVITY

Combining equations 2 and 4:

$$(\varepsilon - \mathrm{I})\mathbf{E} = (1/V)\, \Sigma_k\, \alpha_p(k)\, \mathbf{F}(k), \qquad (1A)$$

where ε (= n^2) is the dielectric constant, in this case a tensor, and I is the identity matrix. Because the density, ρ, is the mass, m, per unit cell volume, V, equation 1A may be rewritten:

$$(\varepsilon - \mathrm{I})/\rho\ \mathbf{E} = (1/m)\, \Sigma_k\, \alpha_p(k)\, \mathbf{F}(k) \qquad (2A)$$

The coefficient $(\varepsilon - \mathrm{I})/\rho$ is the tensor form of the Drude (or Newton-Drude) constant, K_D (*e.g.*, Bloss 1971). Thus the Drude constant has a sound basis in point-dipole theory.

The relationship of point-dipole theory to other optical constants is less useful. For instance, the specific refractivity, K_L, is given by the Lorenz–Lorentz equation (Bloss 1971), and can be related simply to the nontensorial Drude constant:

$$K_D = (\varepsilon + 2)K_L \qquad (3A)$$

This equation extends naturally to tensors, *i.e.*, ε and K_L may both be expressed as tensors. Combining equation 3A with 2A:

$$(\varepsilon + 2)K_L\, \mathbf{E} = (1/m)\, \Sigma_k\, \alpha_p(k)\, \mathbf{F}(k) \qquad (4A)$$

However this equation is of questionable value because it separates otherwise dependent tensors, ε and K_L.

The popular Gladstone–Dale constant (specific refractivity), K_G, can be related to the Drude constant:

$$K_D = (\varepsilon\tfrac{1}{2} + 1)\, K_G \qquad (5A)$$

In this case, it is not clear that the Gladstone–Dale constant has a meaningful tensorial representation. Whereas Gladstone–Dale constants have proven valuable for predicting mean indices of refraction on the basis of composition and density (*e.g.*, Mandarino 1976, 1978, 1979, 1981), there appears to be no extension by which the principal indices of refraction of an anisotropic crystal can be anticipated, nor can the orientation of the indicatrix be predicted.